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THERMAL STABILITY OF EPOXY COMPOSITE MATERIALS

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US ARMY ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING CENTER
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13. ABSTRACT *(Maximum 200 words)*

The thermal oxidative stability of Fiberite 7714A (glass/epoxy), 976 (carbon/epoxy), and 977-2 (carbon/epoxy) was studied at temperatures up to and above their respective glass transition temperatures. Composite samples were subjected to both short- and long-term heating. The first set of samples was heated for 4-6 hours from 100 to 350°C, and the second set of samples was cycled for 30-minute intervals from 200 to 400°C.

The samples were tested in a Perkin-Elmer TGA7 Thermogravimetric Analyzer and weight loss recorded. Weight loss data were compared based on temperature and time at temperature. The results showed good thermal stability for each epoxy material through its glass transition temperature with a weight loss of 1.5% or less. The results were comparable for both long- and short-term temperature exposure.

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INTRODUCTION

Projectile launchers afford a unique application for composite materials. Organic composite materials can be used to increase dimensional stability and stiffness. Polymer blends can increase impact strength and thermal stability. Unlike other high-temperature applications, cannons can withstand both sustained and short-term heating at elevated temperatures. They are frequently fired for relatively short periods of time and undergo repeated cyclic heating. Based on the current and future performance requirements for present and future projectile launchers, a true service temperature for composite materials for each application should be established. Manufacturer specifications generally recommend a maximum service temperature for an extended period of time and do not address any effect experienced by short-term cyclic heating. Depending on the composite system, cannon minimum service temperature requirement of 300°C may exceed the recommended service temperature.

Development of composite structures for use in projectile launchers requires knowledge of thermal degradation of composite materials after continual thermal cycling. Materials may or may not be satisfactory for the thermal application of projectile launchers. Once the thermal stability of a material is established, the effect of degradation on the mechanical properties must be identified to determine a true service temperature.

EXPERIMENTAL PROCEDURE

Test specimens were prepared from three Fiberite resin systems [7714A (glass/epoxy), 976 (carbon/epoxy), and 977-2 (carbon/epoxy)] as specified in the manufacturer's product guide. The specimens were sectioned and analyzed by a Perkin-Elmer Differential Scanning Calorimeter, Model DSC7, to determine their glass transition temperature (Tg). Samples of 10-15 mg were sealed in standard aluminum pans and heated in a nitrogen atmosphere at a scanning rate of 20°C/min. The Tg was determined by extending the pre- and post-transition baseline and taking the midpoint of the transition region.

The thermal stability of each composite material was evaluated in a Perkin-Elmer Thermogravimetric Analyzer, Model TGA7, using a 15-20 mg sample heated in an oxygen atmosphere. Two methods of isothermal analysis were performed to simulate different firing scenarios. First, a set of samples was heated at a rate of 20°C/min to a specific testing temperature, then held at constant temperature; in the case of 7714A, for 4 hours at 100°, 150°, 200°, 250°, and 275°C, while 976 and 977-2 were heated for 6 hours at 200°, 250°, 300°, 325°, and 350°C. Next, a sample set was heated at a rate of 20°C/min, then held at constant temperature (200°, 225°, 250°, and 300°C) for 30 minutes, and cooled at a rate of 20°C/min to 25°C. The procedure was repeated for a total of 12 cycles. In each case, the weight loss was measured for each cycle and temperature.

RESULTS AND DISCUSSION

All three Fiberite prepreg materials analyzed were epoxy resins, reinforced with either glass or carbon fibers (Table 1):

- **Fiberite 7714A**, a brominated epoxy resin with glass fibers, is a flame-resistant polymer with a recommended service temperature of 71°C. The samples had an average resin content of 27.4% and a Tg of 120°C.

- **Fiberite 976** is an epoxy prepreg reinforced with carbon fibers; its recommended service temperature is 177°C. TGA analysis revealed an average resin content of 37.5% and a Tg of 212°C.

- **Fiberite 977-2** is a toughened epoxy/carbon prepreg with a recommended service temperature of 149°C. The prepreg had an average resin content of 35.8% and a Tg of 174°C.

Fiberite 7714A when heated in an oxygen environment for 4 hours at constant temperatures up to 150°C showed good thermal stability with a weight loss of 0.35% (Table 2 and Figure 1). The observed weight loss is most likely the result of a loss in absorbed water. When the temperature was increased from 150°C to 200°C, the weight loss increased to 1.08%, which indicates an onset of thermal decomposition of the sample. When the temperature was increased beyond 200°C, the decomposition of the resin (not the glass fibers) increased dramatically, indicating severe material decomposition.

As seen in Figure 2 and Table 2, when Fiberite 976 was heated in oxygen at a constant temperature of 150°C for 6 hours, the weight loss was approximately the same as that observed in Fiberite 7714A, which had been heated for 4 hours. The weight loss of Fiberite 977-2 was 0.71%, twice that observed in 976. However, when the temperature was increased to 200°C, its weight loss remained constant, while 976 increased to 1.11%. This supports the theory that the observed weight losses up to 150°C were the result of moisture absorption and in the case of 977-2 was probably true up to 200°C. Increasing the temperature to 200°C again showed the onset of thermal decomposition for the 976 resin with 977-2 remaining stable. When the temperature was increased above 200°C, the rate of decomposition increased significantly for both resins.

The second set of samples was subjected to cyclic heating for a total of twelve 30-minute cycles. At 200°C, the 7714A samples showed a cumulative weight loss of 1.64% for 12 cycles (Figure 3 and Table 3); however, 46% of the total weight loss was observed in the first cycle. Increasing the temperature to 225°C showed a 60% increase in the total weight loss; however, the rate of decomposition was almost the same, being displaced only by the increased weight loss observed in the first cycle as seen in Figure 6. When the temperature was increased to 250°C, both the cumulative weight loss and rate of decomposition were dramatically increased. Comparing the 4-hour weight loss with the cumulative weight loss after eight 30-minute cycles showed (Figure 6) that in each case, the weight loss was more severe for cyclic heating than that observed during constant heating.

Fiberite 976 when heated for 12 cycles at 200°C showed a cumulative weight loss of 0.88%, with 48% of the weight loss occurring in the first cycle (Figure 4 and Table 3). Increasing the temperature to 250°C showed a cumulative weight loss of 4.40%, or a 400% increase. The rate of decomposition also showed a large increase. At 300°C, the weight loss increased to 6.32%, and a slight increase in the decomposition rate was observed. Comparing the 6-hour weight loss with the cumulative weight loss after 12 cycles showed that at 250°C and 300°C, the cyclic decomposition was more severe, while at 200°C the cyclic weight loss decreased by 0.23%.

Fiberite 977-2 when heated for 12 cycles at 200°C showed a cumulative weight loss of 0.78%, with 44% of the weight loss resulting from the first heating cycle (Figure 5 and Table 3). Increasing the temperature to 250°C increased the weight loss to 3.52%, or a 450% increase. The rate of decomposition increased but not as much as that observed in the 976 resin. At 300°C, the total weight loss increased to 8.25%, or a 234% increase compared with 250°C. Also, the rate of decomposition showed a large increase. In comparison with the 6-hour weight loss, at 250°C and 300°C, the cyclic weight loss was again much greater; however, at 200°C, the results were almost identical.

CONCLUSION

Fiberite 976 and 977-2 (Figure 6) both showed good thermal stability at 200°C based on both the continual and cyclic heating data. This is 23°C above the recommended service temperature for the former and 51°C above for the latter. The 7714A resin system, however, began to show significant decomposition at this temperature. Based on the 4-hour weight loss data, this material could probably sustain temperatures up to 150°C, which is 70°C above the recommended temperature.

Increasing the temperature to 250°C (Figure 7) increased the material weight loss significantly for all three resins. Fiberite 977-2 showed the best stability, but all three materials showed permanent decomposition.

At 300°C (Figure 8) both 976 and 977-2 showed a substantial weight loss and significant decomposition. Fiberite 7714A was not tested at this temperature for obvious reasons.

In summary, based on the data:

- The onset of thermal decomposition begins between 150°C and 200°C for Fiberite 7714A and 977-2, with decomposition beginning between 200°C and 250°C for 977-2.

- The effect of cyclic heating appeared to be more deleterious to the resin systems than continual heating, once the onset of decomposition begins.

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Table 1: Material properties

RESIN	PREPREG	RECOMMENDED SERV TEMP	Tg	AVE RESIN CONTENT
7714A	Epoxy/glass	71°C		27.4%
976	Epoxy/carbon	177°C	212°C	37.5%
977-2	Epoxy/carbon	174°C	174°C	35.8%

Table 2: Weight loss after 4 or 6 hours at temperature

TEMP (°C)	7714A (4 HRS) WEIGHT LOSS	976 (6 HRS) WEIGHT LOSS	977-2 (6 HRS) WEIGHT LOSS
100	0.35%	NA	NA
150	0.35%	0.34%	0.71%
200	1.08%	1.11%	0.72%
225	1.87%	NA	NA
250	3.29%	2.36%	2.16%
275	4.28%	NA	NA
300	NA	5.76%	5.01%
325	NA	10.85%	9.61%
350	NA	26.34%	22.60%

Table 3: Cumulative weight loss for 12 cycles at 30 min/cycle

CYCLE	7714A 200°C WT. LOSS	7714A 225°C WT. LOSS	7714A 250°C WT. LOSS	976 200°C WT. LOSS	976 250°C WT. LOSS	976 300°C WT. LOSS	977-2 200°C WT. LOSS	977-2 250°C WT. LOSS	977-2 300°C WT. LOSS
1	0.75	1.65	2.42	0.42	1.50	2.66	0.34	1.58	3.46
2	0.90	1.83	2.88	0.54	1.99	3.24	0.41	2.01	4.15
3	1.00	1.93	3.18	0.61	2.35	3.64	0.46	2.28	4.70
4	1.09	2.02	3.46	0.63	2.60	3.93	0.49	2.48	5.16
5	1.19	2.11	3.72	0.68	2.94	4.31	0.54	2.87	5.65
6	1.26	2.20	4.07	0.72	3.20	4.69	0.57	2.97	6.08
7	1.33	2.28	4.29	0.75	3.43	4.97	0.60	3.08	6.49
8	1.39	2.35	4.51	0.77	3.59	5.20	0.62	3.18	6.86
9	1.48	2.42	4.71	0.82	3.95	5.58	0.68	3.30	7.24
10	1.53	2.49	4.86	0.83	4.11	5.82	0.75	3.38	7.58
11	1.59	2.55	4.97	0.86	4.21	6.09	0.77	3.45	7.81
12	1.69	2.60	5.08	0.88	4.40	6.32	0.78	3.52	8.25

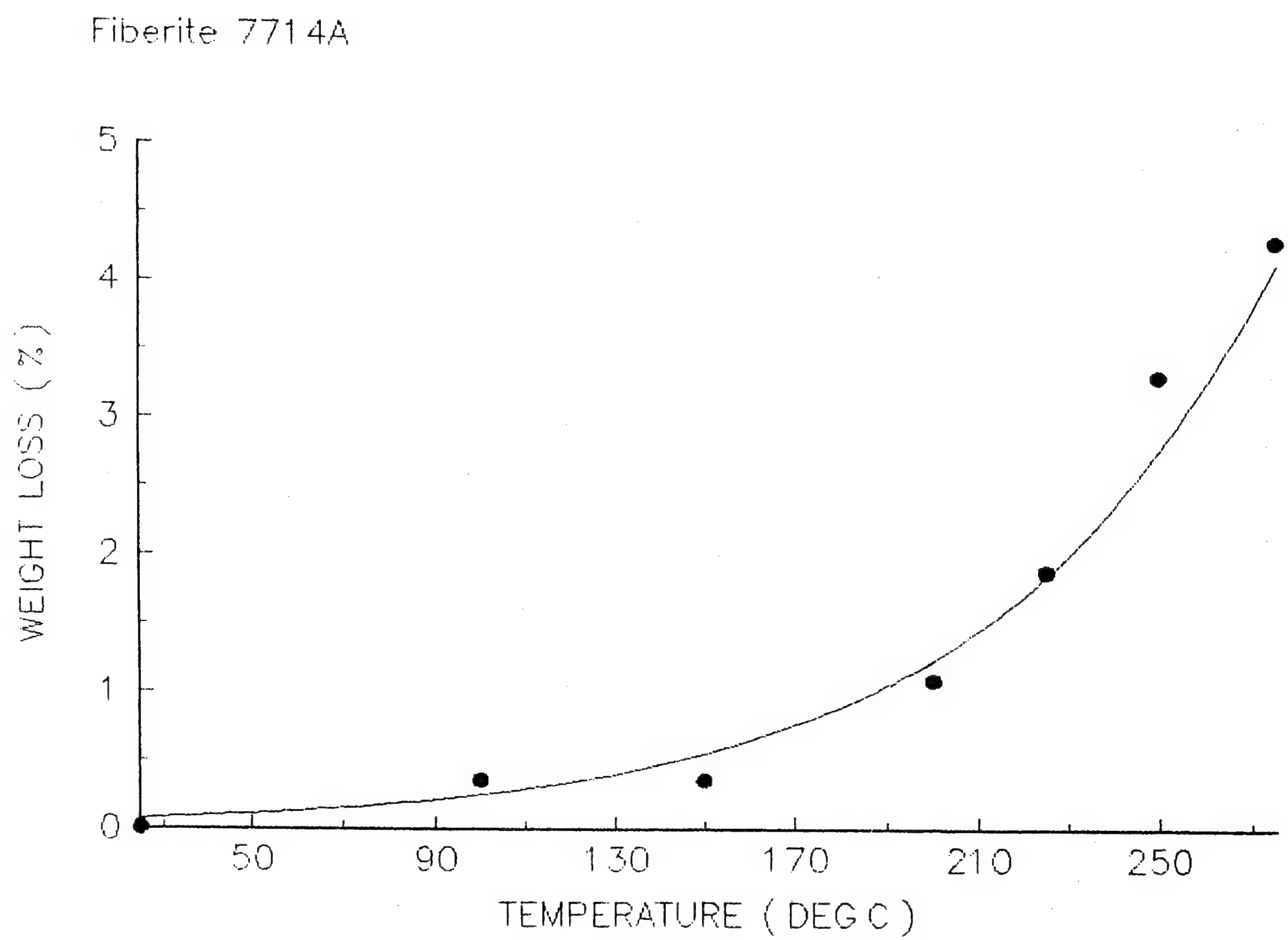

Figure 1. Plot of weight loss after 4 hrs versus temperature

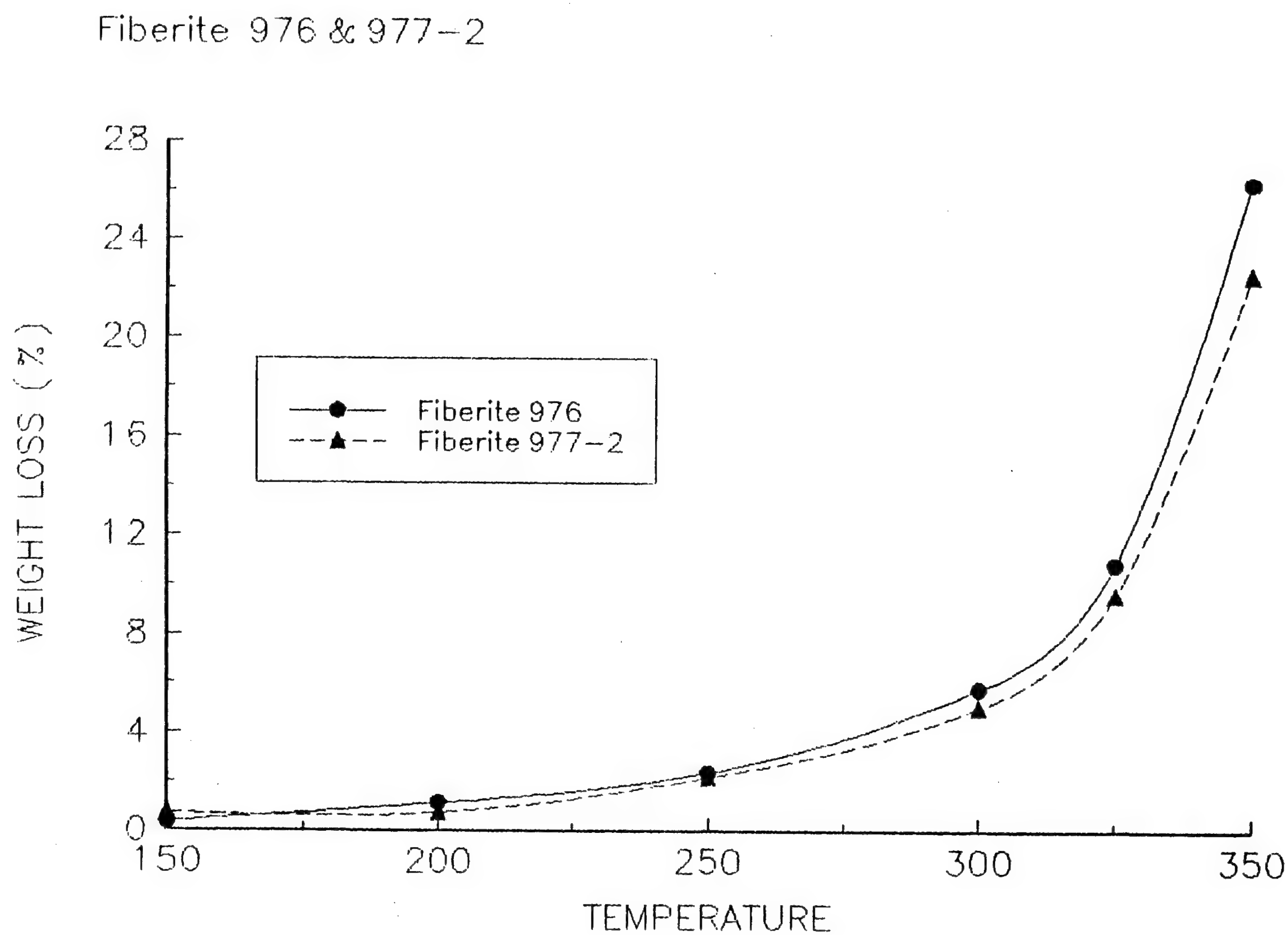

Figure 2. Plot of weight loss after 6 hrs versus temperature

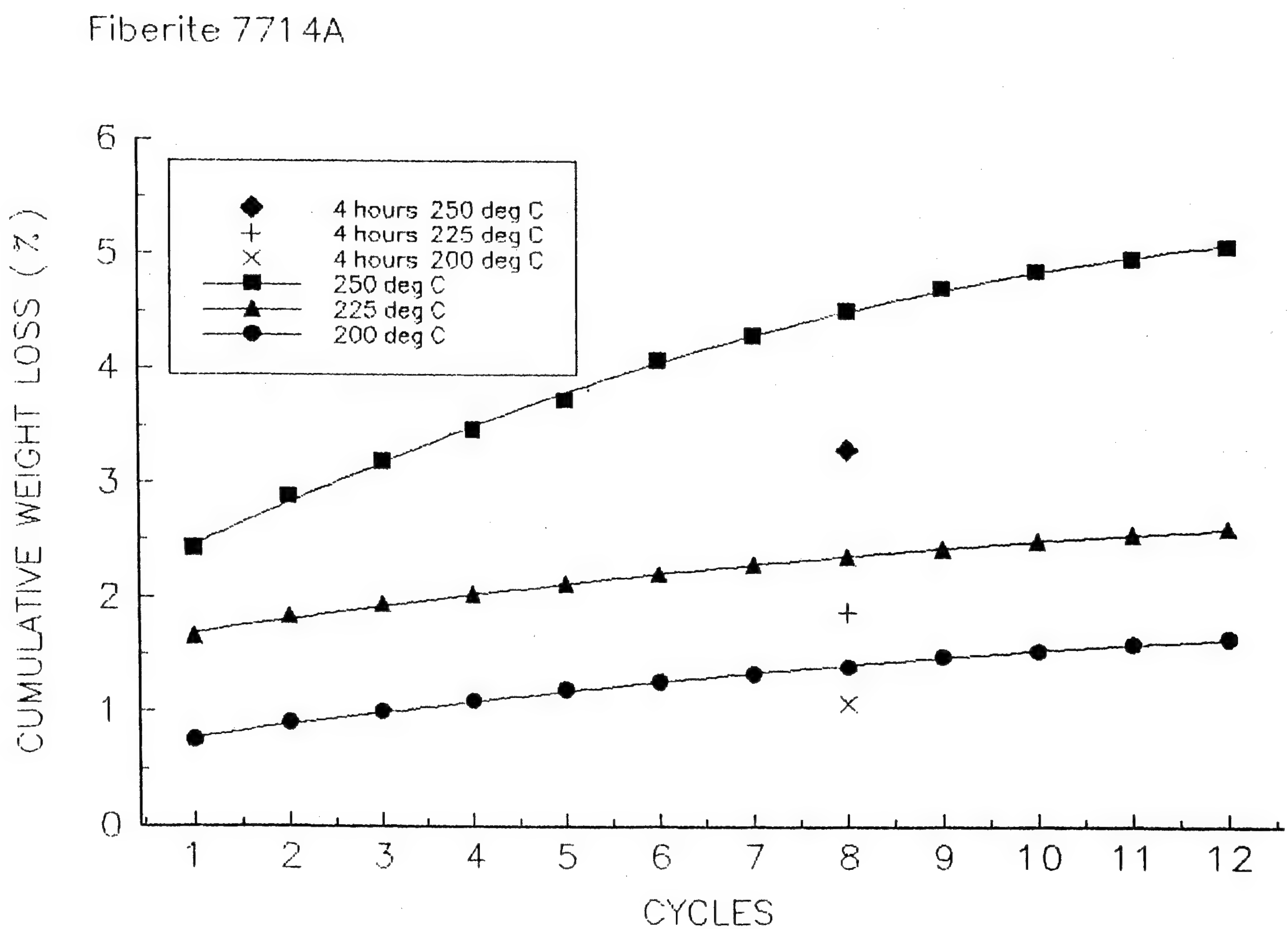

Figure 3. Cumulative weight loss at 200, 225, and 250^{0}C

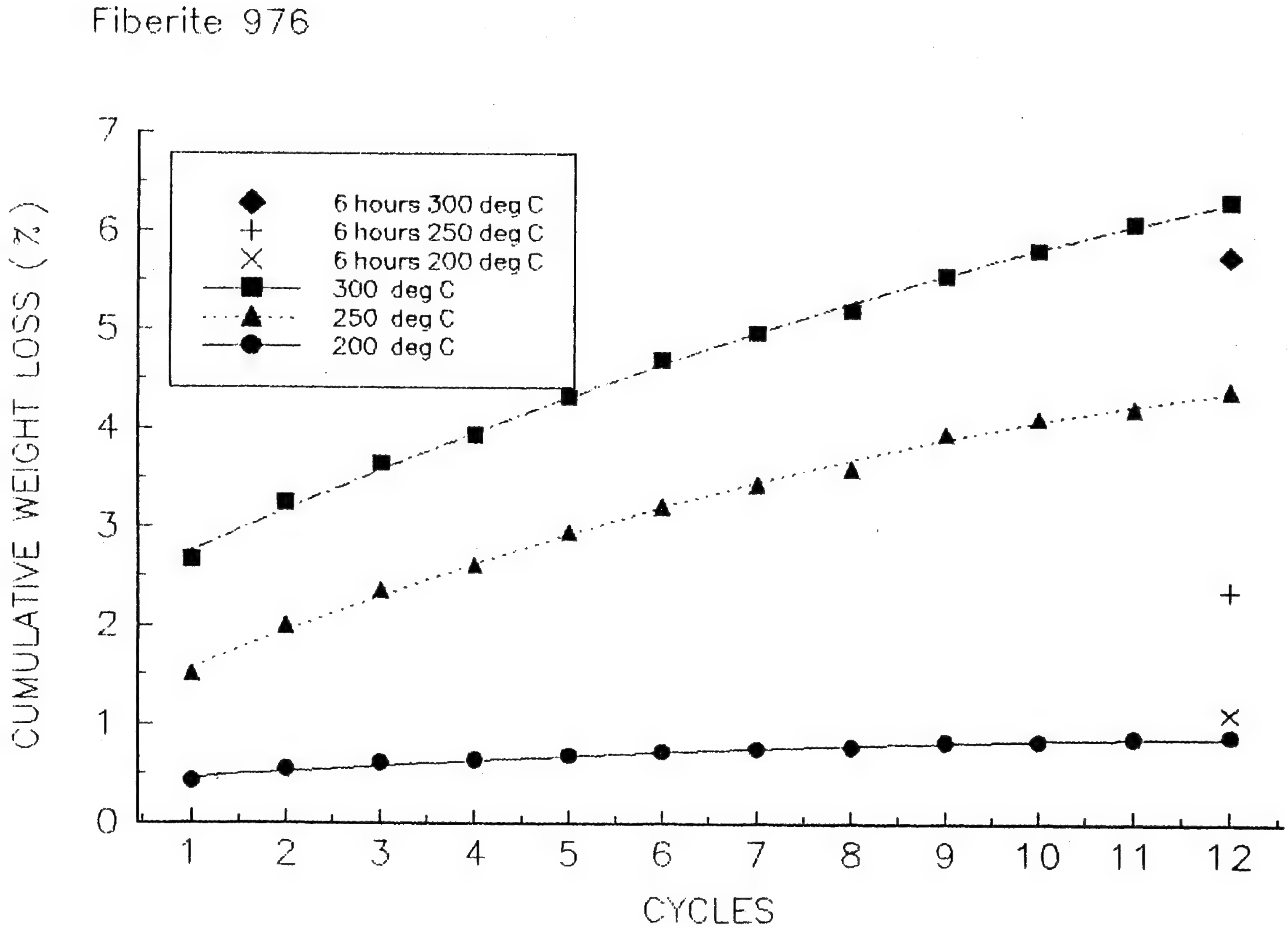

Figure 4. Cumulative weight loss at 200, 250, and 300°C

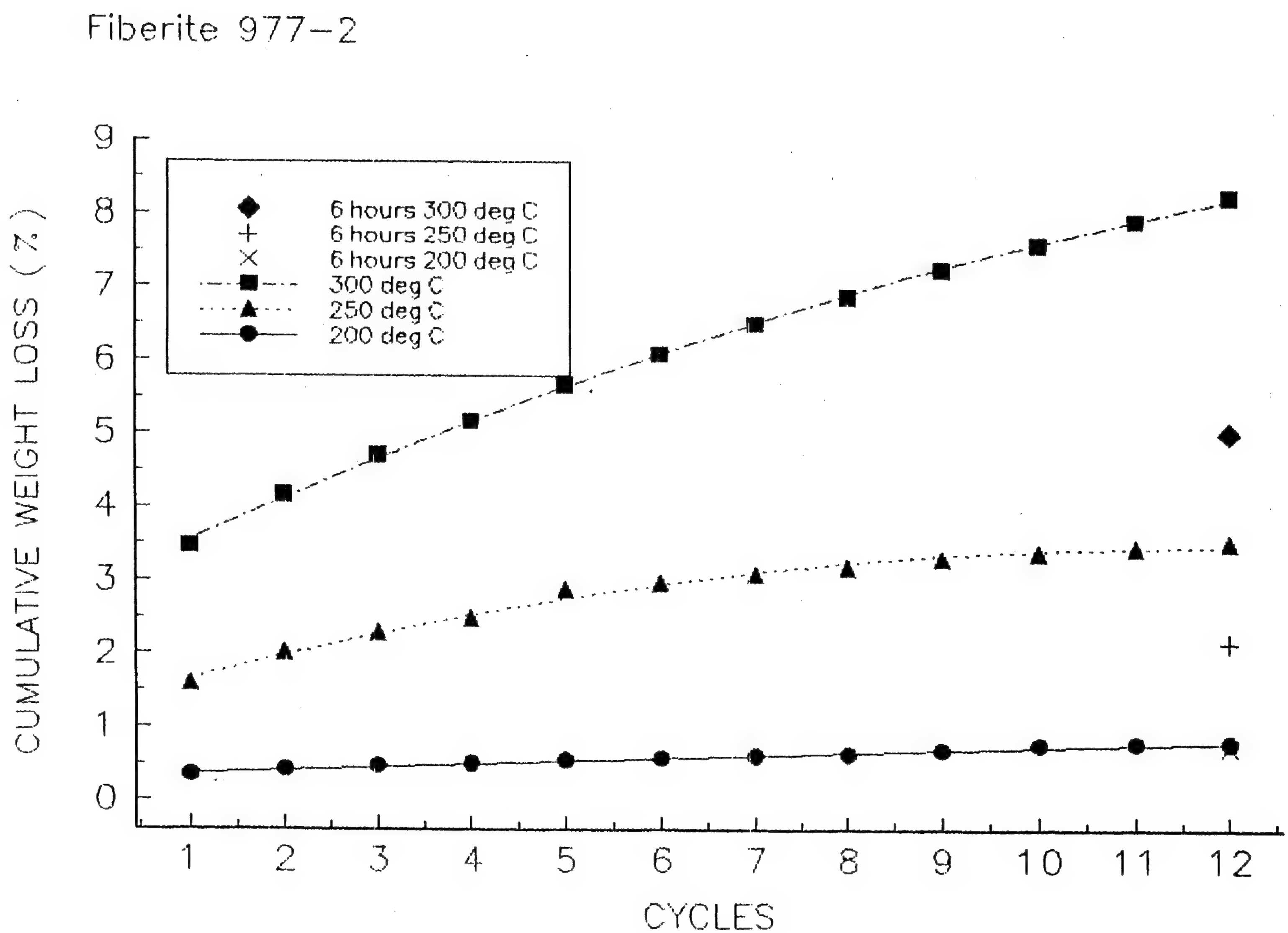

Figure 5. Cumulative weight loss at 200, 250, and 300^{0}C

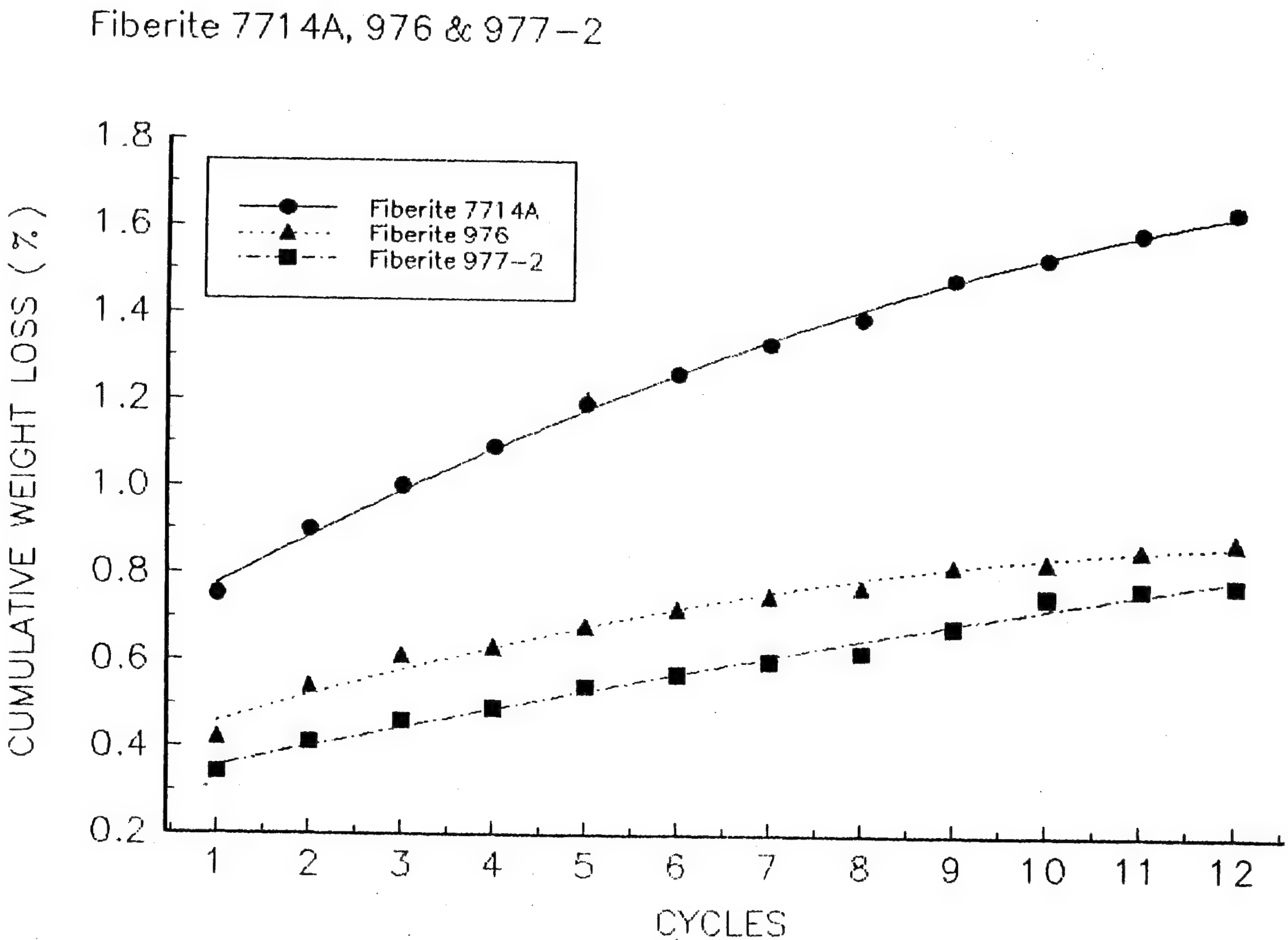

Figure 6. Cumulative weight loss for 7714A, 976, and 977-2 at 200°C

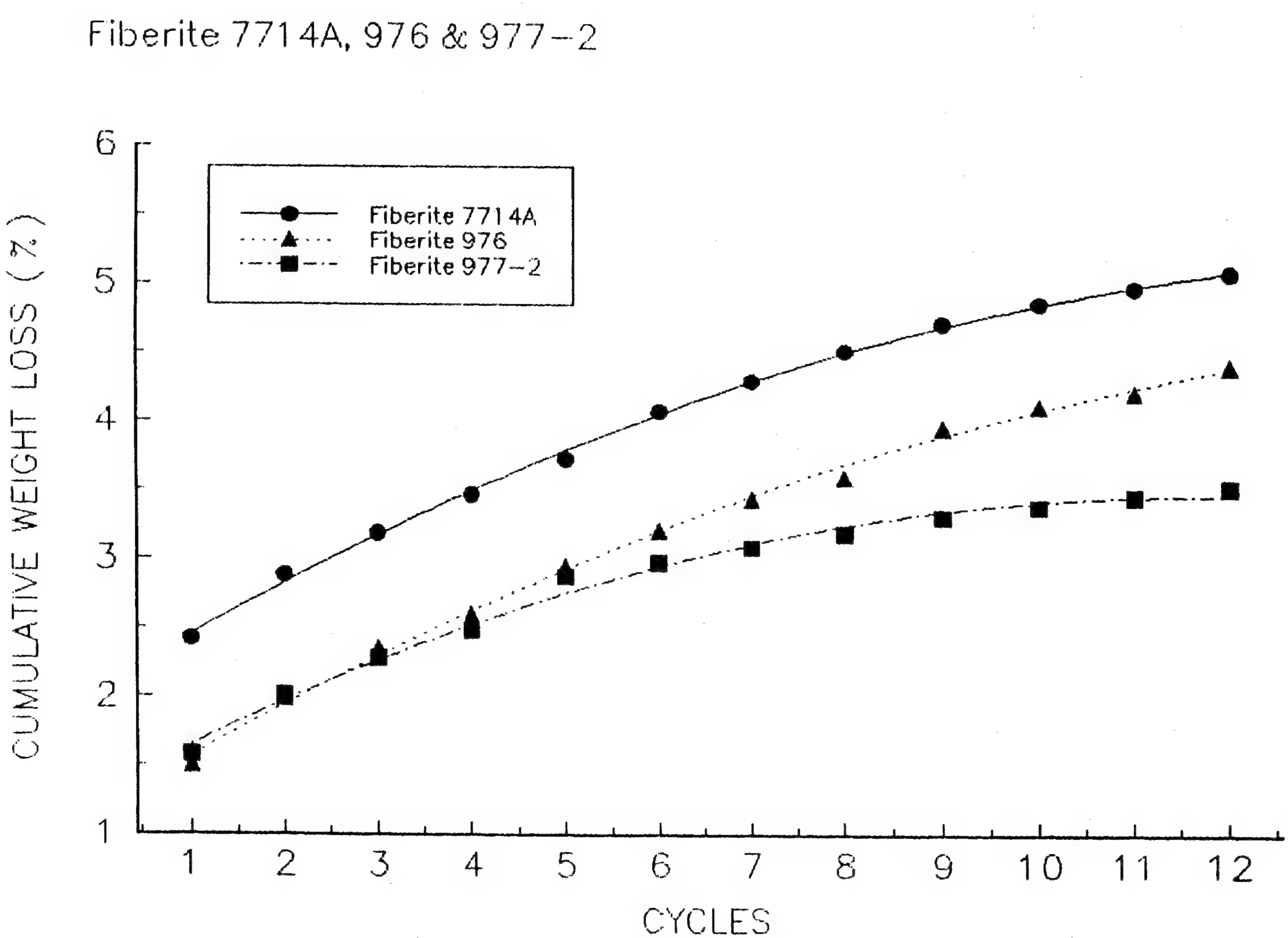

Figure 7. Cumulative weight loss for 7714A, 976, and 977-2 at 250°C

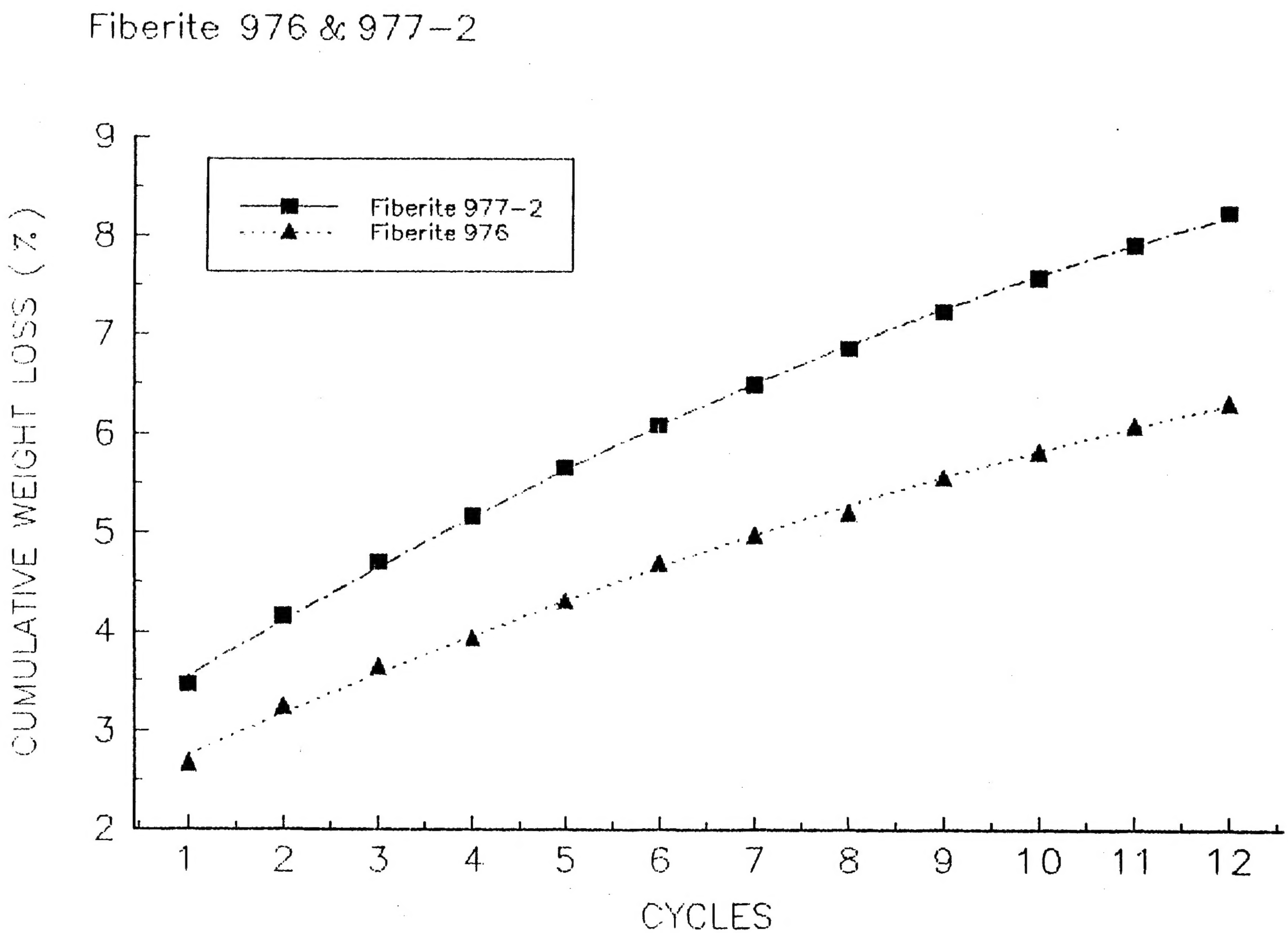

Figure 8. Cumulative weight loss for 976 and 977-2 at 300^{0}C

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